THE CHEMICAL STRUCTURE AND THERMAL MODIFICATION OF LOW RANK COALS

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ABSTRACT

For two brown coals, Australian Yallourn and Indonesian South Banko coals, measurements of SPE/MAS ^{13}C NMR spectra, OH group analysis according to acetylation and silylation, Curie-point pyrolysis, and analysis of CO_2H groups were conducted. Based on these results, plausible chemical structural units of above brown coals were proposed and submitted to CAMD calculation to understand the interactive forces of units. On the other hand, these brown coals were found to show the higher reactivities when modified in the presence of water at around 350 °C. The enhancement of these reactivities was examined by supposing what kinds of reaction take place based on the unit chemical structures proposed here and the interactive forces of these units.

INTRODUCTION

In 1987, Hüttinger *et al.* had proposed molecular structure of a typical Rheinishe brown coal based on elemental analysis, pyrolysis experiments, and extrapolation of literature data and successfully explained the pyrolysis and hydropyrolysis data of brown coals [1]. In 1992, Hatcher *et al.* [2] and Nomura *et al.* [3] proposed chemical structural units of subbituminous coal and bituminous coal by applying solid state NMR data in the combination with conventional data such as from pyrolysis and quantification of functional groups, respectively. Nomura *et al.* pointed out the importance of the following subjects concerning the elucidation of chemical structure of coals: (1) more precise and quantitative evaluation of chemical bonds connecting aromatic rings; (2) search for analysis of constituents without accompanying coke formation; (3) reliable evaluation of real molecular weight of extracts; (4) research on qualitative and quantitative evaluation of non-bonding interactions in coal organic matrix; (5) study on the quantitativeness of CP/MAS ^{13}C NMR spectroscopy. These mean that, around 1992, these subjects remain uncertain. As for subject (1), Stock *et al.* proposed RuO_4 oxidation method as the means to evaluate aliphatic substituents on aromatic rings [4]. In this RuO_4 oxidation, aliphatic portion connecting aromatic rings could be converted to aliphatic dicarboxylic acid derivatives; This experiments showed that there were many different kinds of aliphatic dicarboxylic acids even though their amounts are so small. [5] However, the presence and amount of methylene bridge could not be detected and quantified by this method because resulting malonic acid is unstable under the reaction conditions. Solid state ^{13}C NMR is still powerful means, suggesting the distribution of different kinds of carbon contained in coal organic matrix. At present time, SPE/MAS ^{13}C NMR spectra are believed to be more quantitative than CP/MAS ^{13}C NMR spectra [6]. The advantage of using ^{13}C NMR spectral data for the evaluation of unit chemical structure is that the spectra can reflect the whole coal. As for subject (2) and (3) there has been no rapid progress since 1992. As for subject (4), much attention are paid to non-bonding interactions in coal organic matrix, however, there is few method to evaluate them in the quantitative way. Authors are now thinking that non-bonding interaction might be very important to consider the reaction taking place at the early stage of heating process. In that sense, the unit chemical structures proposed here and their non-bonding interactions based on CAMD study give us the meaningful clues to understand the reactivities of brown coal at the early stage of liquefaction and thermally modified brown coal.

EXPERIMENTAL SECTION

Coal samples. Two brown coals, Australian Yallourn and Indonesian South Banko coals (YL and SB), were employed in this study, which were provided by the curtsey of Nippon Brown Coal Liquefaction Co. Ltd. These were ground under 200 mesh and dried at 40 °C in vacuo before use. Elemental analysis of these two coals are listed in Table 1.

Consecutive extraction and acetylation of THF-insoluble materials. A dried and pulverized coal samples (5 g) was put in a Soxhlet thimble, then being set in the apparatus. Extraction with tetrahydrofuran (THF) was conducted for one day. The resulting residue (THF-insoluble materials) was submitted to acetylation by refluxing in a solvent mixture of acetic anhydride-pyridine, then the acetylated samples being extracted again with THF. These procedures were repeated for three times (scheme of this extraction is shown in Figure 1). The resulting products were submitted to structural analysis according to GPC.

Solid state* ^{13}C *NMR measurement. CP/MAS and SPE/MAS ^{13}C NMR spectra were recorded on a Chemmagnetic CMX-300 with MAS method (10 kHz). For the measurement, about 150 mg of coal were packed in a vessel (5 mm diameter x 8 mm long). The experimental conditions employed were as follows; 200 s pulse delay, 45° pulse width, and *ca.* 400 scan number. Deconvolution of the spectra was conducted on an Apple Macintosh computer with a commercial NMR data processing software, MacAlice (ver 2.0, JEOL Datum). The resulting spectra were divided into twelve Gaussian curves. For two brown coals, Yallourn and South Banko coals, SPE/MAS (Figure 2) and CP/MAS gave following *fa* values, 0.77 and 0.66, and 0.60 and 0.54, respectively.

Diffuse reflectance FT/IR (DR/FT/IR) measurement. Dried sample (50 mg) and KBr (450 mg) were mixed and ground by using an agate mortar. The resulting mixture was further

dried at 90 °C for 10 h in vacuo. FT/IR spectrum of the sample was recorded on a JEOL JIR-AQS20M with diffuse reflectance method (128 scans). Data acquisition and analysis were also carried out on the computer equipped with the spectrometer.

Gel permeation chromatography. Analysis by gel permeation chromatography (GPC) was conducted by using a Shimadzu LC-10AS liquid chromatographic system with a Shodex KF-80M GPC column (30 cm, stationary phase: polystyrene gel) and a Shimadzu SPD-10A ultraviolet detector (λ=270 nm). An extract (6.3 mg) was dissolved in 10 mL of DMF, 20 μL of which was injected to the LC system, when either DMF or lithium bromide-containing DMF was used as eluant. Calibration of retention time-molecular weight relationships was conducted by using 14 kinds of standard polystyrene samples and benzene.

Quantitative analysis of OH groups. (1) Acetylation Method: According to the method reported by Blom *et al.* [7], analysis of OH groups was conducted. (2) Silylation method: According to the Friedman's method [8], we conducted silylation of coal. The details are referred in his paper.

Quantitative analysis of CO_2H groups. These analysis were conducted by ion exchange with sodium acetate [9] and ion exchange with sodium bicarbonate.

Computer simulation. Computer simulation was conducted on an Apple Power Macintosh personal computer by using a commercial CAMD (computer-aided molecular design) software, CAChe (CAChe Scientific, Inc., Version 3.7). At first, the structure proposed in this study was input to a computer, then, molecular mechanics (MM) calculation being conducted till root-mean-square error becomes less than 0.1 kcal/mol. Then, molecular dynamics (MD) calculation was carried out for 10 ps to avoid local minimum structure. From this calculation, intermediary conformers were output every 0.1 ps. Consequently, 100 conformers could be obtained, among which five lowest energy conformers were selected and submitted to MM calculation. At last, we selected the conformer having the lowest energy and defined it as the most reliable conformer.

RESULTS AND DISCUSSION

Construction of unit chemical structures of coals. As we cited already in the experimental section, SPE/MAS ^{13}C NMR spectra were found to give higher *fa* value than CP/MAS ^{13}C NMR spectra. From the carbon distribution based on ^{13}C NMR, we found that α-methylene is more abundant in SB coal compared with YL coal, this indicating that SB coal is rich in methylene, polymethylene and more alkyl groups substituted on aromatic rings.

In brown coal, due to the presence of a lot of hydroxyl groups, hydrogen bonding interaction should be more significant, especially in constructing three dimensionally complicated structure. First of all, we extracted two brown coals by THF under refluxing conditions. In order to obtain much more amount of coal extract, we conducted consecutive extraction of residue after acetylation. As we pointed out the importance of molecular weight information of coal, we submitted these extracts to GPC where we found the following interesting phenomena: the use of LiBr-containing DMF as eluant, seems to be able to dissociate extracts due to breakage of hydrogen bonding. This experiments informed us of the molecular weight of the extract being around from 4000 to 6000 with the maximum peaks. Based on these findings, we firstly assumed average molecular weight of brown coals around 5000. Basing on elemental analysis and above molecular weight, following molecules are proposed for each coal; YL $C_{279}H_{235}N_2O_{87}$ and SB $C_{297}H_{270}N_4SO_{67}$. From *fa* values based on SPE/MAS ^{13}C NMR spectra, numbers of aromatic carbons in each unit are decided to be 215 for YL and 196 for SB. As for the constituents of aromatics in coal, Curie-point pyrolysis data (at 670 °C for 3 s) were referred to. As for the aliphatic portion, we have to conduct RuO_4 oxidation even if at present time it is not quantitative, however, in this study we consulted the NMR data, which can give the distribution of different carbons in coal. By referring to the data on oxygen-containing groups, we tentatively proposed following numbers of each group in unit structure: YL -OH 31, -CO_2H 12, -CO_2Ar 6, -O- 38; SB -OH 28, -CO_2H 7, -CO_2Ar 4, -O- 29. Table 1 is the comparison of calculated values of models and observed values of original coals. These two models are submitted to computer simulation (Figure 3).

Computer simulation. Computer simulation of model structures was carried out using molecular mechanics and molecular dynamics in order to obtain the most stable conformation. Each energy term for the coal structural model for brown coals is listed in Table 2. As for potential energy, YL model was found to show a higher negative value than that of SB model, indicating that YL coal is more stable than SB coal. It is interesting to note that non-covalent bonding energy is higher negative value than covalent bonding energy in both models. Higher negative non-covalent bonding energy with YL model is indicating that hydrogen bonding is prevailing in this coal. We conducted liquefaction of two brown coals here and found that SB coal showed higher reactivity than YL coal (higher hexane soluble portion). At the early stage of liquefaction, OH groups are believed to play important roles in the reactivity. If we consider that YL coal, due to it high contribution of intermolecular hydrogen boding, tends to conduct condensation reaction to a great extent, the resulting lower yield of lighter fraction could be explained in a reasonable way. In Japan, low rank coal is now processed around 350 °C in the presence of water using an 8.4t/day pilot plant, the resultant coals showing good reactivities. The reactivity of modified coal could be rationalized in this context. We are now conducting the measurements of FT/IR, swelling index and SEM observation of these modified brown coals to examine their properties.

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Table 1. Comparison of calculated values of model and observed values of original coal with two brown coals

Yalloum coal	South Banko coal
Ultimate analysis (wt%, daf)	Ultimate analysis (wt%, daf)
C H N S O	C H N S O
67.1 4.7 0.6 0 27.6	70.7 5.8 1.1 0.7 21.7
(66.9)(4.7) (0.5) (0.3) (27.6)	(71.3)(5.4) (1.2) (0.5) (21.6)
Oxygen-containing functional groups (wt%, daf)	Oxygen-containing functional groups (wt%, daf)
-OH 10.37 (10.46)	-OH 9.32 (9.44)
-COOH 10.60 (11.02)	-COOH 6.39 (5.94)
Carbon aromaticity, fa	Carbon aromaticity, fa
0.78 (0.77)	0.69 (0.66)

Table 2. Each energy term for the coal structural model for brown coals

Energy term	YL	SB
total	-732.977	-604.096
Covalent bonding	-227.871	-158.460
stretch	11.432	11.972
angle	129.207	154.672
stretch bend	0.188	0.355
dihedral	-370.588	-326.310
improp tortion	1.888	0.850
Non-covalent bonding	-505.106	-445.636
electrostatics	-69.811	-42.020
van der waals	33.205	-14.801
hydrogen bond	-468.500	-388.815

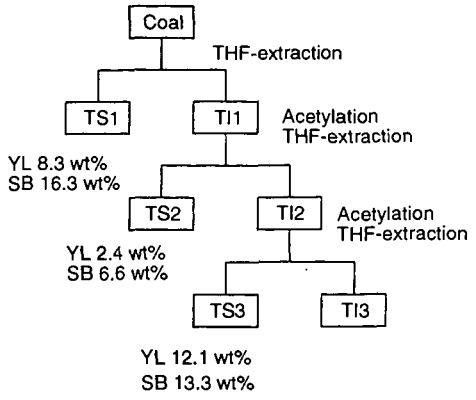

Figure 1. Procedure for consecutive extraction of two brown coals.

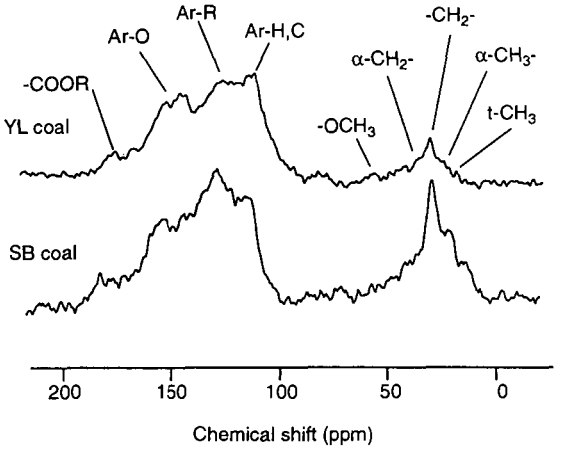

Figure 2. SPE/MAS ^{13}C NMR of two brown coals

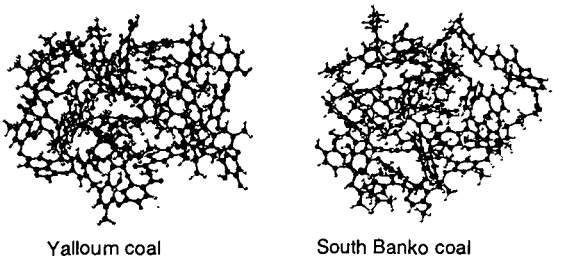

Figure 3. 3D skecth for the model structures proposed